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Light induced exchange energy transfer reactions of micelle forming Ru(II) diimine complexes

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Abstract

Photoinduced energy transfer from two surfactant Ru(II) diimine complexes of the type $[(bpy)_2Ru(L)]^{2+}$ (L = 4-methyl-4′-heptadecyl-2,2′-bipyridine and 4,4′-diheptadecyl-2,2′-bipyridine) to anthracene-9-carboxylate (ANC) was investigated in aqueous solutions of the complexes. The luminescence quenching behavior of both complexes is strongly dependent on the complex concentration in solution and the ionic strength of the solution. The complexes exhibit a 20 nm red shift of the emission maximum upon micelle formation; the emission spectral changes illustrate the dependence of the critical micelle concentration (cmc) on the solution ionic strength. The quenching of the micellized complexes by ANC is dramatically enhanced relative to the complex in the aqueous phase. The dynamics of exchange energy transfer quenching of the micellized complex can be evaluated assuming a Poisson distribution of ANC quenchers among the micellized complex. The ^{3}[ANC] formed in the quenching process can escape the micelle and react by electron transfer quenching with methyl viologen in the aqueous phase.

Keywords: Light-induced exchange; Energy transfer reactions; Ruthenium complexes; Diimine complexes; Micelle complexes

1. Introduction

A central characteristic of artificial photosynthetic systems is the ability to efficiently absorb visible light and funnel the excitation energy to a reactive center. In recent years much effort has been directed toward the development of artificial light harvesting systems which can be used to convert sunlight into electrical or chemical potential [1–3]. Formation of molecular micro-environments by concentration of light absorbing antennae or induced self-assembly of chromophores provides an avenue for creating arrays of molecules capable of rapid sensitization of a site where excited state electron transfer can occur. A relatively simple way to concentrate chromophores is through the use of micelle forming surfactants which will associate sensitizing and reactive chromophores via ion-pairing or hydrophobic interactions. There are numerous examples of photoinduced electron transfer reactions in micelles [4,5], but only a limited number of examples exist where micelles are employed in a light harvesting capacity. For instance, Scaiano and Selwyn made use of sodium dodecyl sulfate micelles to concentrate ketones such as acetophenone and propiophenone as sensitizers for γ-methylvalerophenone which decomposes via a Norrish type II process following excitation by energy transfer [6]. This system concentrates light harvesting and reactive components in the micelle to enhance the efficiency of the sensitization process.

A more intriguing concept concerns the use of micelles consisting of light absorbing surfactants as sensitizers for reactive centers incorporated in the micelle via hydrophobic or electrostatic interactions. Such polychromophoric aggregates may serve as effective light harvesting arrays if excitonic migration or self-exchange energy transfer processes within the array are efficient. Shahinan and Bagdasarian explored the concept of cooperative resonance energy migration in alkyl sulfate micelles [7] following UV absorption. Others have shown that various cyanine dyes aggregate at low concentration in aqueous solutions to produce aggregates with unique optical properties [8]; however, photoreactivity of the materials was not examined.

Among inorganic chromophores it has been shown that surfactant derivatives of Ru(II) tris(2,2′-bipyridyl) self-assemble to form micelles in aqueous solutions. Grätzel examined the complex $[(bpy)_2Ru(DC13)]Cl_2$ (DC13 = 4,4′-ditridecyl-2,2′-bipyridine; bpy = 2,2′-bipyridine) and found that *N*-methylphenothiazine, MPTH, efficiently quenches the luminescence of the micellized chromophores by reductive electron transfer (Eq. (1)) [9]. The MPTH radical cation is expelled from the

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$$[(bpy)_2Ru(DC13)]^{2+}* + MPTH \longrightarrow [(bpy)_2Ru(DC13)]^{+} + MPTH^{+} \quad (1)$$

micelle and the subsequent charge recombination reaction is several orders of magnitude slower than in homogeneous solutions (below the critical micelle concentration). In earlier work [10] we reported the physical properties of a variety of surfactant Ru(II) bipyridyl complexes $[(bpy)_2R(L)]Cl_2$ where L was one of 4,4′-diheptadecyl-2,2′-bipyridyl (DC17), 4-methyl-4′-heptadecyl-2,2′-bipyridine (MC17) and 4,4′-ditridecyl-2,2′-bipyridine (DC13). It was shown that luminescence quenching of the complexes with methyl viologen, MV^{2+}, is observed only with chromophores *not* incorporated into micelles. Bimolecular quenching of the micellized complexes is too slow to compete with excited state relaxation. In addition, escape of excited chromophores from the micellar phase is slow relative to excited state relaxation in these systems.

The possibility of micellized Ru(II) complexes serving as light harvesting arrays is explored in this work. A critical issue is whether or not self-exchange energy migration occurs efficiently between adjacent chromophores in the micellar array of chromophores. One means of addressing this is to examine the dynamics of quenching of micelles with quenchers that associate with the micelles via hydrophobic or ion-pairing interactions. In this work we report results of exchange energy transfer quenching of surfactant complexes of MC17 and DC17 with anthracene-9-carboxylic acid (ANC) which associates with the micelles.

2. Experimental

2.1. Materials

The ligands MC17, DC17, DC13 and complexes of the type $[(bpy)_2Ru(L)]Cl_2$ were prepared as previously reported [10]. The ligand MC5 (4-methyl-4′-pentyl-2,2′-bipyridine) and $[(bpy)_2Ru(MC5)]Cl_2$ were prepared by methods identical to those used for the long chain bipyridines [10]. Anthracene-9-carboxylic acid was obtained from Aldrich Chemical Co. and used without further purification. Buffers used in this work were prepared from KH_2PO_4 and K_2HPO_4 (Fisher) of the highest quality commercially available; trace impurities of various anions in the buffer can act as luminescence quenchers of the micellized complexes.

2.2. Physical studies

All absorption spectra were taken using a HP8452 diode array spectrophotometer. Emission spectra were measured using a SPEX Instruments model 111 photon counting fluorimeter equipped with a cooled PMT housing (with Hamamatsu R928 PMT), 450 W Xe Arc lamp and a controlled temperature sample holder. Slits were maintained to provide a resolution of <2 nm. Spectra were not corrected for PMT response. Relative luminescence quantum yields were obtained using $[Ru(bpy)_3]Cl_2$ in aerated H_2O as reference. The excitation wavelength for all relative yield measurements was chosen so that the absorbance of the reference and sample was less than 0.4. Steady state luminescence quenching experiments were performed by mixing buffered solutions of complex and freshly prepared ANC solutions. The solutions were not deaerated and emission spectra were obtained immediately following mixing. Higher quality data was obtained in undegassed solutions since bubbling and or FPT degassing result in slight loss of complex due to foaming.

Luminescence lifetimes were obtained using time correlated single photon counting (TCSPC). The apparatus included an IBH Instruments model flashlamp filled with hydrogen with a Schott glass UG-1 filter for the flashlamp emission. Luminescence was detected at right angles using an Andover Co. narrow band pass filter (610 ± 5 nm) at the entrance of a Pacific Inst. cooled PMT housing (with Hamamatsu R929 PMT with power from Bertan 325 supply). Output of the PMT was directed to a Comlinear model 500 MHz preamplifier prior to input of the signal to a Tennelec model TC 454 constant fraction discriminator (CFD). A start pulse from the flashlamp was independently directed to the CFD. The frequency of discriminated luminescence was maintained at a level $\leqslant 1\%$ of the flashlamp frequency. Output of the CFD was directed to a Tennelec model TC 863 TAC and the TAC signal served as input to a Viking Instruments MCA in a Gateway microcomputer (Intel 80486, 25 MHz). Luminescence decays were analyzed using in-house software which employs a modified Marquardt algorithm for analysis of single and double exponential decays.

Transient absorption spectra were obtained at the University of New Orleans, in the laboratory of Dr Piotr Protrowiak. Sample excitation was with the second harmonic (532 nm) of a Continuum Nd:YAG laser (approx. 10 mJ/pulse). The absorbance was monitored using the output of a Hamamatsu flashlamp directed through the sample before filtering with an Oriel monochromator and detection with a Hamamatsu R928 PMT output to a Tektronix Transient digitizer. Laser, flashlamp and digitizer triggering was controlled using a Stanford Instruments delay generator.

3. Results and discussion

3.1. Luminescence spectra

In previous work the cmc values for the $[(bpy)_2Ru(L)]^{2+}$ complexes of MC17, MC13 and DC13

were reported [9,10]. In addition, the ionic strength dependence of the cmc of $[(bpy)_2Ru(MC17)]Cl_2$ was examined. Micellization of this complex is accompanied by a 20 nm red shift in the maximum of the metal-to-ligand charge transfer luminescence. Similar shifts are observed in the luminescence of $[Ru(bpy)_3]^{2+}$ bound to sodium dodecyl sulfate (SDS) micelles [11]. Fig. 1 shows the ionic strength dependence of the complex concentration range over which the emission maximum shift occurs for $[(bpy)_2Ru(MC17)]^{2+}$; the Fig. also notes critical micelle concentrations obtained from surface tensiometry at two different ionic strengths. In the absence of added electrolyte, micellization occurs at concentrations typical of surfactants having a single alkyl chain and a divalent head group. The cmc measured by surface tensiometry is at the onset of the shift in the luminescence maximum. As the ionic strength is increased the red shift in the luminescence maximum occurs at lower complex concentrations. In 0.5 M phosphate buffered to pH 7 the cmc determined by surface tensiometry is at a complex concentration where the luminescence spectral shift is complete; the difference may reflect the relative sensitivity of surface tensiometry in detecting aggregation in very dilute solutions. If the onset of the luminescence spectral change is taken to be the cmc, the values for $[(bpy)_2Ru(MC17)]^{2+}$ in solutions having 0, 0.05 and 0.5 M phosphate are 7×10^{-4}, 1×10^{-5} and 5×10^{-6} M, respectively. Thus aggregation of chromophores occurs even in very dilute buffered solutions.

The reactivity of $[(bpy)_2Ru(DC17)]^{2+}$ will also be discussed in this work. This complex is not soluble in solutions lacking supporting electrolyte and has a luminescence maximum of 635 nm at all measurable concentrations ($>10^{-7}$ M) in pH 7 phosphate solutions.

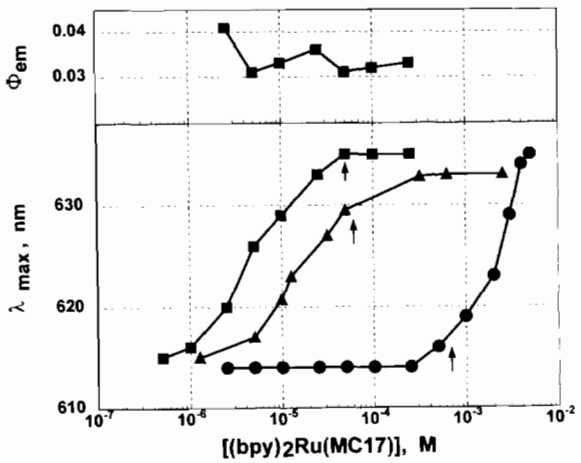


Fig. 1. Luminescence maximum vs. $[(bpy)_2Ru(MC17)]^{2+}$ in solutions containing 0 (●), 0.05 (▲) and 0.5 (■) M phosphate buffered to pH 7. Critical micelle concentrations obtained by surface tensiometry are marked with arrows. The emission quantum yield, Φ_{em}, as a function of $[(bpy)_2Ru(MC17)]^{2+}$ concentration is also shown.

Very likely this complex aggregates at extremely low concentrations.

3.2. Luminescence quantum yields and decays

Previous reports of association of $[Ru(bpy)_3]^{2+}$ with sodium dodecyl sulfate (SDS) micelles showed that, at pre-micellar concentrations of SDS, aggregates of $[Ru(bpy)_3]^{2+}$ ion-paired with SDS exist which exhibit efficient self-quenching of the MLCT luminescence of the complex [12,13]. The luminescence decays of $[Ru(bpy)_3]^{2+}$ are complex multiple exponentials in these solutions. Above the cmc of SDS, the $[Ru(bpy)_3]^{2+}$ chromophores are sufficiently dilute that no self-quenching occurs [14,15].

For $[(bpy)_2Ru(MC17)]^{2+}$ luminescence quantum yields were measured in aerated solutions as a function of complex concentration in 0.5 M phosphate solutions as shown in Fig. 1. A slight decrease in the relative emission yield is observed with increasing complex concentration. Luminescence decays of dilute solutions of the complex ($<10^{-5}$ M) in the absence of added electrolyte are single exponential but are multiple exponential in the presence of concentrated electrolyte (Fig. 2). The complexity of luminescence decays in the absence of specific added quenchers suggests some degree of self-quenching or quenching by impurities associated with the buffer which strongly associate with the aggregated complex. Analysis of luminescence decays in the presence of added quenchers is limited by the complexity associated with 'unquenched' solutions of the complex. Despite the complex decay kinetics the degree of self-quenching and impurity quenching is relatively small; the luminescence quantum yield for $[(bpy)_2Ru(MC17)]^{2+}$ decreases by no more than 30%.

3.3. Quenching with anthracene-9-carboxylate

The MLCT excited state of Ru(II) diimine complexes has been shown to react by single electron transfer, singlet energy transfer and triplet energy transfer paths

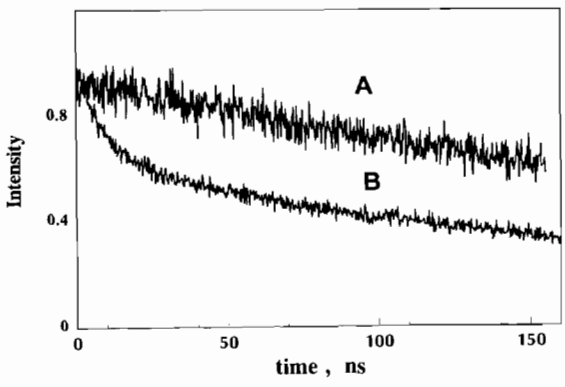


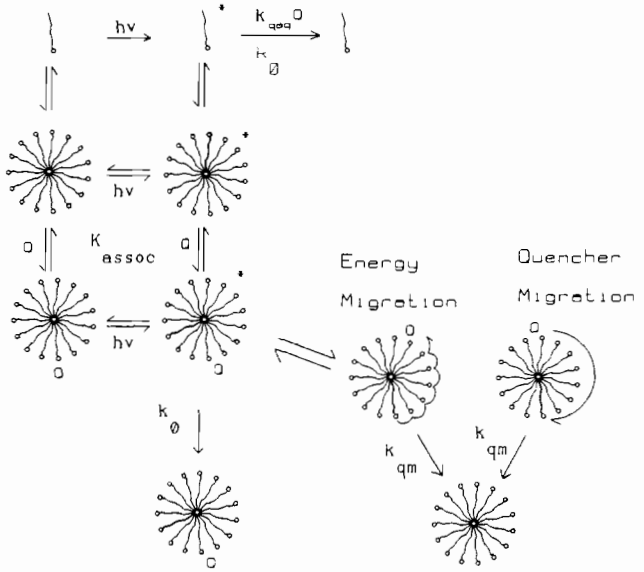
Fig. 2. Luminescence decays of $[(bpy)_2Ru(MC17)]^{2+}$ (50 μM) in solutions containing 0 (A) and 0.5 M (B) phosphate buffered to pH 7.

[16–18]. Meyer and co-workers have shown that numerous Ru(II) and Os(II) diimine complexes are readily quenched by anthracene and anthracene derivatives via triplet energy transfer (Eq. (2)) with rate constants approaching diffusion limited values [19]. In addition they established that the energy transfer occurs by an electron exchange mechanism and that theories used to describe non-adiabatic electron transfer reactions

$$[Ru]^{3}* + AN \xrightarrow{k_{en}} [Ru] + [AN]^{3}* \quad (2)$$

can be used to evaluate the free energy dependence of the energy transfer process. By using ANC as a quencher in aqueous solutions of the surfactant complexes, the possibility of quencher ion pairing interactions with the micelle exists. The micelles can then serve as light harvesting arrays to sensitize the ANC. Scheme 1 illustrates one possible mechanism for the process. The ANC ion pairs with the micelles in the ground state to some degree and quenching of the complex in both the aqueous and micellar phases can occur. A key requirement for light harvesting in Scheme 1 is either migration of excitation energy on the micelle surface or quencher migration. The result would be enhancement of the quenching relative to solutions lacking chromophore–quencher ion-pair formation.

Fig. 3 shows the degree of emission quenching (I_0/I) as a function of ANC concentration for $[(bpy)_2Ru(DC17)]^{2+}$, $[(bpy)_2Ru(MC17)]^{2+}$, $[(bpy)_2Ru(MC5)]^{2+}$ and $[Ru(dmb)_3]^{2+}$ (dmb = 4,4′-dimethyl-2,2′-bipyridine) at two different complex concentrations. At both complex concentrations neither $[Ru(dmb)_3]^{2+}$ nor $[(bpy)_2Ru(MC5)]^{2+}$ are quenched ($I_0/I \approx 1$) at ANC concentrations below 0.5 mM. The rate constant for quenching of $[Ru(dmb)_3]^{2+}$ by ANC is 2×10^9 M^{-1} s^{-1}, and is independent of complex concentration. The



Scheme 1.

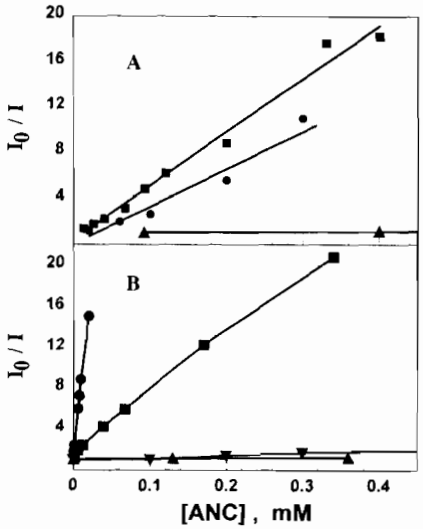


Fig. 3. Luminescence quenching of $[(bpy)_2Ru(MC17)]^{2+}$ (■), $[(bpy)_2Ru(DC17)]^{2+}$ (●), $[(bpy)_2Ru(MC5)]^{2+}$ (▼) and $[Ru(dmb)_3]^{2+}$ (▲) expressed as I_0/I vs. [ANC] at complex concentrations of 1 mM (A) and 8 μM (B) in 0.5 M phosphate buffer at pH 7.

Table 1
Data from quenching of complexes with ANC in 0.5 M pH 7 buffered solutions

Complex	[Complex]	K_{sv} rel[a] (M^{-1})	cmc[b] (M)	m[b]
$[Ru(dmb)_3]^{2+}$	8 μM, 1 mM	1		
$[(bpy)_2Ru(MC5)]^{2+}$	8 μM, 1 mM	1.3		
$[(bpy)_2Ru(MC17)]^{2+}$	8 μM	70	8×10^{-5}	38
	1 mM	56		
$[(bpy)_2Ru(DC17)]^{2+}$	8 μM	990	2×10^{-7}	20
	1 mM	25		

[a]Determined using the Stern–Volmer relationship, $I_0/I = 1 + K_{sv}[ANC]$.

[b]Determined from fits of data to Eq. (7) assuming $K_{assoc} = 20000$ M^{-1}, $k_{qaq} = 4\times10^{10}$ M^{-1} s^{-1} and $k_{qm} = 5\times10^{6}$ s^{-1}.

complex having a short alkyl chain, $[Ru(MC5)]^{2+}$, exhibits similar quenching. By contrast both $[(bpy)_2Ru(MC17)]^{2+}$ and $[(bpy)_2Ru(DC17)]^{2+}$ are nearly completely quenched in 0.5 mM ANC at complex concentrations of 8 μM and 1 mM. The Stern–Volmer quenching curves of Fig. 3 are not linear for the two surfactant complexes. Both complexes show upward curvature with increasing ANS concentration. Stern–Volmer quenching constants from linear fits of the data of Fig. 3 are shown in Table 1. The constants indicate the relative increase in the degree of quenching of the two surfactant complexes at surfactant concentrations of 8 μM and 1 mM. The relative quenching constant increases by more than a factor of 25 for both surfactants in all cases.

Examination of Scheme 1 indicates that luminescence occurs from the surfactant complex both in micelles and in the aqueous phase. Since quenching of complexes in the aqueous phase is much slower than quenching

of the micellized complex, and previous results indicate exchange is slow, a simple Stern–Volmer like relationship can be written in which the observed quenching ratio is the sum of the reaction of the surfactant in the aqueous and micellar phases (Eq. (3)).

$$I_0/I_{obs} = \left[\alpha_{mic} \left(\frac{k_r + k_n}{k_r + k_n + k_{qm}[Ru,ANC]_{mic}} \right) + (1 - \alpha_{mic}) \left(\frac{k_r + k_n}{k_r + k_n + k_{qaq}[ANC]_{aq}} \right) \right]^{-1} \quad (3)$$

where α_{mic} is the fraction of micellized surfactant ([complex] − cmc/[complex]) and $[Ru,ANC]_{mic}$ is the concentration of ANC bound to micelles. It is assumed that the radiative and non-radiative decay rate constants ($k_r + k_n$) of the complex are the same in aqueous and micellar phases. Since quenching of the aqueous complex is negligible at the ANC concentrations studied, luminescence from surfactant in the aqueous phase would result in a plateau in curves of I_0/I versus [ANC]. The fact that no plateau is observed for quenching in solutions having 8 μM complex suggests the cmc (non-micellized surfactant) is much lower than this value ($< 8 \times 10^{-7}$ M).

The observed enhancement of luminescence quenching (Fig. 3) could arise from a variety of factors including (i) increased local concentration of ANC in the micellar phase, (ii) local concentration enhancement and quencher migration on the micelle surface, and (iii) local concentration and migration of excitation energy between adjacent chromophores via self-exchange energy transfer. Quenching ratios in solutions having 1 mM complex indicate that greater than 90% of excited $[(bpy)_2Ru(MC17)]^{2+}$ is quenched when the solution contains an ANC:$[(bpy)_2Ru(MC17)]^{2+}$ ratio of 1:4. Each complex in the micelle is likely to have at least four nearest neighbors; thus, on average, no chromophore is more than one exchange site away from a quencher.

If no migration of excitation energy or quencher occurs in the micelles only static quenching can occur. Since the energy transfer mechanism in this system is exchange energy transfer, the rate constant for energy transfer should fall off exponentially with distance [20] and static quenching processes should be efficient only for the $[(bpy)_2Ru(MC17)]$/ANC ion-pair or next nearest neighbor in the micelle.

Substitution of surfactant complex with another cationic surfactant should not change the quenching efficiency if the process is purely static but would dramatically affect quenching if exciton migration or self-exchange energy transfer is involved in the quenching process. Fig. 4 shows the effect of dilution of $[(bpy)_2Ru(MC17)]^{2+}$ with cetyltrimethyl ammonium bromide (CTAB); the total surfactant concentration is maintained at 2 mM. While the slope of the plot decreases upon increasing the CTAB concentration,

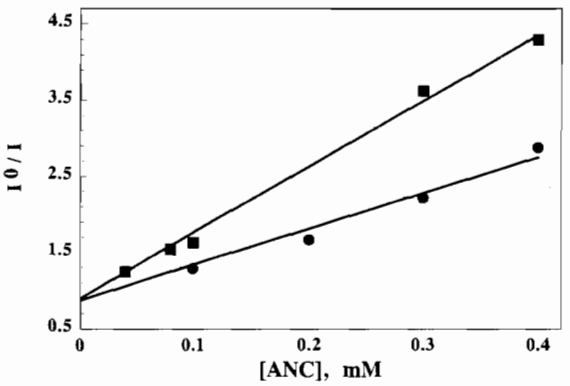


Fig. 4. Quenching of $[(bpy)_2Ru(MC17)]^{2+}$ by ANC in solutions containing 2 mM $[(bpy)_2Ru(MC17)]^{2+}$ (■) and 1 mM $[(bpy)_2Ru(MC17)]^{2+}$ + 1 mM CTAB (●). Solutions are buffered (0.5 M) to pH 7.

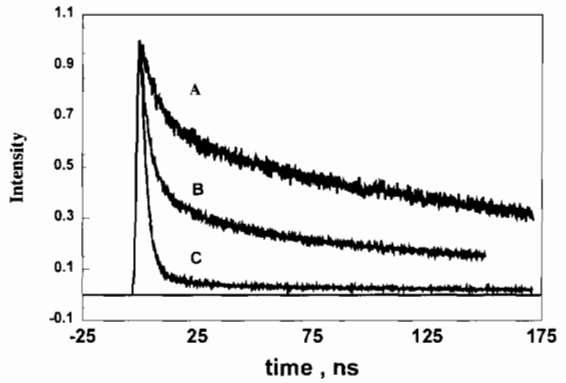


Fig. 5. Luminescence decays of $[(bpy)_2Ru(MC17)]^{2+}$ (8 μM) in pH 7 phosphate buffer (0.5 M) containing 0 M (A), 1×10^{-5} M (B) and 1×10^{-4} M (C) ANC.

the effect is relatively small and may simply reflect a decrease in the equilibrium constant for association of ANC with the cationic micelles. The observed behavior strongly suggests that migration of the excitation energy by self-exchange energy transfer does *not* contribute significantly to the overall quenching reaction.

Purely static quenching of the micellized complex luminescence should result in double exponential luminescence decays with a rapidly decaying component associated with the metal complex/ANC ion-pair and a long lived luminescence from the unquenched complex. Fig. 5 clearly shows that this is not the case. While there is always a short and long lived component to the decay, the rate constant for both decays clearly changes as the quencher concentration increases. This dynamic behavior could be the result of (i) quenching by collision of ANC in the aqueous phase with the micelle or (ii) migration of micelle bound ANC on or within the micelle. Since the ANC concentrations required to completely quench the luminescence are low, even diffusion limited quenching ($\sim 10^{10}$ M^{-1} s^{-1}) by ANC in the aqueous phase is not fast enough for a bimolecular quenching mechanism to account for the observed behavior. Thus the luminescence decay be-

havior observed with increasing ANC concentration suggests ANC migration contributes to the observed behavior.

3.4. Quantitative treatment of ANC quenching

Assuming the quenching reaction follows Scheme 1, several factors are important in influencing the overall efficiency of energy transfer including (i) the equilibrium constant for association of the ANC with the micelles, K_{assoc}, (ii) the distribution of quenchers among the micelles, (iii) the first-order rate constant for intramicellar quenching, k_{qm}, and (iv) the rate constant for quenching of the complex in the aqueous phase, k_{qaq}. In addition, physical properties of the micelle such as the aggregation number (m) and critical micelle concentration (cmc) are important in determining the average number of quencher molecules bound per micelle and the degree of free chromophore available for solution quenching.

In the model we employed, pre-equilibrium association of ANC with micelles of uniform size is assumed and ion-pairing of ANC with non-micellized chromophores is not considered. The latter assumption is reasonable since little quenching of $[Ru(dmb)_3]^{2+}$ by ANC is observed at the quencher concentrations used and there is no other evidence of ground state complex formation (i.e. spectrophotometric changes). By evaluating the equilibrium of ANC with micellized surfactant (Eq. (4)), the concentration of ANC in the aqueous, $[ANC]_{aq}$, and micellar, $[Ru,ANC]_{mic}$, phases can be determined at any given concentration of ANC and surfactant complex. The equilibrium expression arbitrarily limits the association to one ANC per micellized complex, though multiple ion-pairing is possible. The fraction of micellized chromophores ion-paired to ANC is determined by the equilibrium of Eq. (4).

$$ANC_{aq} + [Ru]_{mic} \rightleftharpoons [Ru,ANC]_{mic} \qquad K_{assoc} \qquad (4)$$

In describing quenching of micellized chromophores we employed a modified version of the model derived by Infelta et al. [21] (and elaborated by others [22–24]) which assumes a Poisson distribution of quenchers among the micelles. The model is particularly useful for cases where the rate constant for intramicellar quenching, k_{qm}, is close in magnitude to the non-radiative decay rate of the excited micellized chromophore, k_0. The Poisson distribution of quenchers in the micelles, expressed as a fraction of micelles having i quenchers, γ_i, is given by Eq. (5).

$$\gamma_i = {n_A}^i \exp(-n_A)/i! \qquad (5)$$

The average number of quenchers per micelle, n_A, can be determined from the concentration of micellized surfactant, $[Ru,ANC]_{mic}$, the total surfactant complex concentration, $[Ru]_T$, the aggregation number of the micelles, m, and the cmc of the surfactant complex (Eq. (6)). With the expression for the average number of quenchers per micelle, the fraction of surfactant

$$n_A = \frac{[Ru,ANC]_{mic} + m}{[Ru]_T - cmc} \qquad (6)$$

complex in the aqueous phase $(1-\alpha)$, and the Infelta model for micellar quenching, a quenching expression can be written which includes both quenching in the aqueous and micellar phases, Eq. (7), where $k_0 = k_r + k_n$.

$$I_0/I = \left[\alpha \left[\frac{k_0}{k_{qm}} \exp(-n_A) \sum \frac{{n_A}^i}{[k_0/k_{qm} + i]i!} \right] + (1-\alpha)\left(\frac{k_0}{k_0 + k_{qaq}[ANC]_{aq}} \right) \right]^{-1} \qquad (7)$$

The first term on the right hand side expresses quenching of chromophores in the micellar phase and the second term is bimolecular quenching in aqueous solution.

Several approximations were made in using Eq. (7) to fit quenching data for $[(bpy)_2Ru(MC17)]^{2+}$ and $[(bpy)_2Ru(DC17)]^{2+}$. It was assumed that the equilibrium constant for association of ANC with the surfactant chromophore was the same for both surfactant complexes examined. In addition, the rate constants for aqueous and micellar quenching, k_{qaq} and k_{qm}, were assumed to be the same for the two surfactants. With these global parameters, the data of Fig. 3 were fit using Eq. (7) by varying the cmc and aggregation number for each surfactant. Results of the fits are shown in Fig. 6 and the values of cmc and aggregation number used in the fits are given in Table 1. The constants

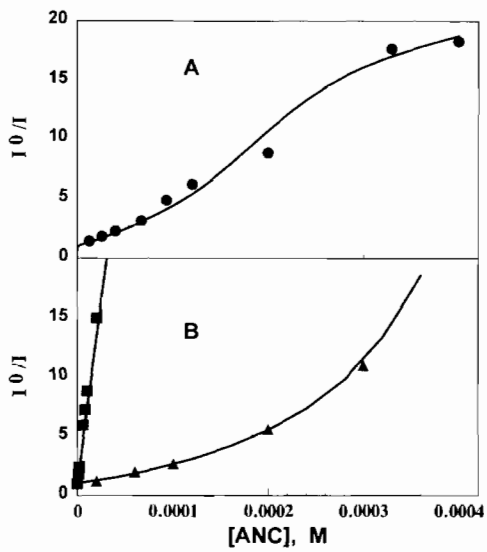


Fig. 6. Luminescence quenching ratios for 1 mM $[(bpy)_2Ru(MC17)]^{2+}$ (A) and $[(bpy)_2Ru(DC17)]^{2+}$ (B) at complex concentrations of 8 μM (■) and 1 mM (▲). Solid lines represent fits to data using Eq. (7) and values of $K_{assoc} = 20\,000\ M^{-1}$, $k_q = 5\times10^6\ s^{-1}$, $k_{qaq} = 4\times10^{10}\ M^{-1}\ s^{-1}$.

used in the fits were 20 000 M^{-1} for K_{assoc}, 5×10^6 s^{-1} for k_{qm} and 4×10^{10} M^{-1} s^{-1} for k_{qaq}. The large value of K_{assoc} is required to fit the quenching of 8 μM $[(bpy)_2Ru(DC17)]^{2+}$ and the relatively low intramicellar quenching rate constant is required to provide the large difference in the degree of quenching observed at the two $[(bpy)_2Ru(DC17)]^{2+}$ concentrations. The value of k_{qm} is nearly the same as the value used for k_0 (3×10^6 s^{-1}); the intramicellar quenching rate constant includes migration of the quencher on the surface of the micelles. The data for 1 mM $[(bpy)_2Ru(MC17)]^{2+}$ is best fit using a cmc of 8×10^{-5} M which is close to the value determined using surface tensiometry. The data obtained using 8 μM $[(bpy)_2Ru(MC17)]^{2+}$ could not be fitted using these parameters and no set of parameters was found that was suitable for fitting all of the quenching curves. A possible explanation for this is that $[(bpy)_2Ru(MC17)]^{2+}$ was neither completely micellized or completely in the aqueous phase at a concentration of 8 μM. Such solutions may exhibit changes in physical properties such as the cmc or aggregation number of existing aggregates upon addition of small quantities of hydrophobic electrolytes which are likely to ion-pair with micellized surfactant. As a result, fixed values of the cmc and aggregation number cannot be assumed in fitting quenching data. We are presently examining this possibility further.

The overall results of these limited quenching studies illustrate that numerous factors influence luminescence quenching of surfactant transition metal complex chromophores. For the purposes of light harvesting the colloidal solutions are attractive since an enormous enhancement in the efficiency of quenching occurs. The most efficient of these systems are those which are completely aggregated at low concentrations and for which the equilibrium constant for quencher association with the surfactant is large; in this case the surfactant with two alkyl chains appeared to be aggregated at all concentrations studied. Since the degree of aggregation depends intimately on the solution properties (i.e. see Fig. 1), the light harvesting efficiency of solutions can be controlled by varying the type and concentration of spectator ions.

3.5. Excited state reaction of the ANC triplet

A number of possibilities exist for using the ^{3}ANC formed in the quenching reaction of Scheme 1. If sensitized ^{3}ANC can escape the micelle during its excited state lifetime, it can react with species in the aqueous phase. One possibility is oxidative quenching of ^{3}ANC to produce the neutral ANC radical; Eq. (8) shows an example using methyl viologen as quencher. Meyer

$$[ANC^-]^3 + MV^{2+} \longrightarrow [ANC^{\cdot}] + MV^+ \quad (8)$$

and co-workers have shown that triplet 9-methylanthracene reacts with methyl viologen by electron transfer [25]. The ANC radical produced in the reaction may exist either as a carboxyl radical, $ANCOO^{\cdot}$ or as a zwitterion, $AN^+COO^{\cdot-}$. In either case association of the oxidized ANC with the micelles following oxidative electron transfer could result in long lived charge separated species with MV^+ remaining in the aqueous phase. To investigate this possibility nanosecond transient absorption spectra were obtained to follow the quenching of the excited surfactant Ru complex and subsequent fate of the ^{3}ANC.

The transient spectrum of $[(bpy)_2Ru(MC17)]^{2+}$ following 532 nm excitation shows excited state absorption with a maximum near 360 nm and ground state bleaching between 400 and 475 nm (Fig. 7(A)); the behavior is very similar to that of $[Ru(bpy)_3]$ and other related chromophores which have been reported [26,27]. Addition of ANC at concentrations high enough to nearly completely quench the luminescence of $[(bpy)_2Ru(MC17)]^{2+}$ yields a transient absorption spectrum with a maximum at approximately 430 nm (Fig. 7(B)); the 360 nm absorption and ground state bleaching of the surfactant complex are not observed at times as short as 10 ns following excitation. The spectrum obtained is characteristic of the triplet state of anthracene and anthracene derivatives [28]. The decay

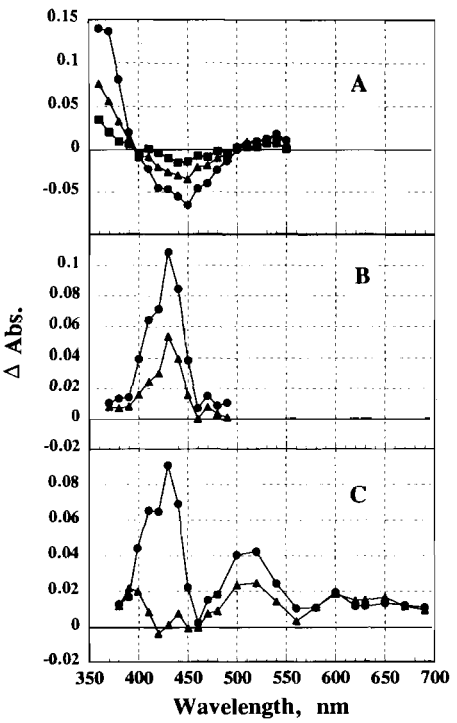


Fig. 7. Transient absorption spectra following 532 nm excitation of 0.5 mM $[(bpy)_2Ru(MC17)]^{2+}$ (A), 0.5 mM $[(bpy)_2Ru(MC17)]^{2+}$ + 0.5 mM ANC (B) and 0.5 mM $[(bpy)_2Ru(MC17)]^{2+}$ + 0.5 mM ANC + 0.01 M MV^{2+} (C). Spectra are shown at 200 ns (●), 400 ns, (▲) and 500 ns (■) following excitation for A, 200 ns (●) and 400 ns (▲) for B and 200 ns (●) and 700 ns (▲) for C.

of the ^{3}[ANC] excited state has two components as shown in Fig. 8; the spectra of the two components have the same absorption features. We are presently investigating this behavior in greater detail.

Pulsed excitation at 532 nm of a solution containing $[(bpy)_2Ru(MC17)]^{2+}$, ANC and methyl viologen, MV^{2+} (0.01 M), exhibits the absorption spectral changes shown in Fig. 7(C). At short times following the excitation pulse (200 ns), the spectrum has features characteristic of ^{3}[ANC]. At several wavelengths the decay has a long lived component ($\tau \gg 1$ μs) as shown in Fig. 8 for absorbance at 600 nm. The long lived component of the ^{3}ANC absorbance at 430 nm is not present in the presence of MV^{2+}. Examination of the spectrum reveals that the absorbance of the ^{3}[ANC] decays rapidly (430–460 nm) but that absorbance persists at shorter wavelengths (<410 nm) and at longer wavelengths. In particular, no change in the absorbance is observed after 200 ns between 370 and 390 nm and between 590 and 700 nm. The viologen radical cation has absorption bands in both these wavelength regions. Direct oxidation of the micellized Ru complex by MV^{2+} is not likely since (i) previous results have shown that the rate constant for quenching of micellized $[(bpy)_2Ru(MC17)]$ by MV^{2+} is negligible and (ii) no bleaching of the complex absorbance between 400 and 500 nm is observed in the transient spectrum (Fig. 7(C)). Assignment of the absorbance between 490 and 550 nm is not clear but may be due to absorption of the oxidized ANC (either as the zwitterion or the neutral radical).

An approximation of the fraction of ^{3}ANC which reacts to yield charge separated radical ions (Eq. (8)) can be made using the transient spectral data. By assuming the molar absorptivity of ^{3}[ANC] at its maximum of 430 nm has a value typical of anthracene triplet (60 000 M^{-1} cm^{-1}) and that ^{3}[ANC] is the only absorbing species at that wavelength following energy transfer from the surfactant complex sensitizer, the concentration of anthracene triplets formed in the laser pulse can be approximated. Given that MV^+ is the only absorbing species at 610 nm ($\epsilon = 11\,000$ M^{-1} cm^{-1}) at long times following excitation, the concentration of viologen radicals can be determined and the fraction of ^{3}[ANC] which reacts to reduce MV^{2+} can be estimated to be greater than 80%.

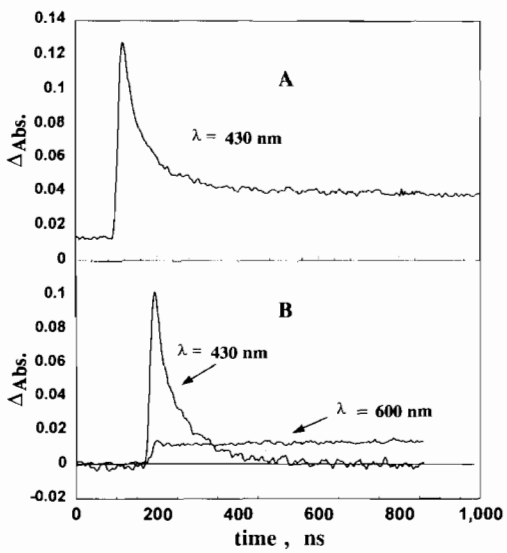


Fig. 8. Decays of transient absorbance following 532 nm excitation of solutions containing 0.5 mM $[(bpy)_2Ru(MC17)]^{2+}$ + 0.5 mM ANC (A) and 0.5 mM $[(bpy)_2Ru(MC17)]^{2+}$ + 0.5 mM ANC + 0.01 M MV^{2+} (B).

While the results obtained to date are not conclusive, preliminary laser flash photolysis experiments suggest the surfactant Ru complex/ANC system may provide a very efficient means of creating charge separated radical ions (in this case oxidized ANC and reduced MV^{2+}). We are currently investigating the dynamics of recombination of the radical ions and the overall efficiency of the process as a function of the degree of micellization of the surfactant complexes.

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